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Center, 4-33, Imafuku 3 chome, Joto-ku, Osaka-
shi**(54) [Title of the Invention] Method for Producing Polyurethane Resin****Aqueous Dispersion****(57) [Summary]**

[Structure] An object of the present invention is to provide a method for easily producing a polyurethane resin aqueous dispersion without using an organic solvent such as acetone or methyl ethyl ketone.

[Effect] A method wherein an isocyanate-capped urethane prepolymer is manufactured and subsequently subjected to a step (1), in which the carboxyl groups are neutralized using a basic compound; and an aqueous dispersion step (2) and a chain-extending step (3), which are performed simultaneously or in succession, thereby producing a polyurethane resin aqueous dispersion, the prepolymer containing a carboxyl group and comprising a diisocyanate compound and a diol compound containing a polymeric polyol. The method being characterized in further comprising a step (4) for diluting the urethane prepolymer using a monoalcohol-based solvent before the aqueous dispersion step (2) is performed.

[Claims]

[Claim 1] A method wherein an isocyanate-capped urethane prepolymer is manufactured, and subsequently subjected to a step (1), in which the carboxyl groups are neutralized using a basic compound; and an aqueous dispersion step (2) and a chain-extending step (3), which are performed simultaneously or in succession, thereby producing a polyurethane resin aqueous dispersion; the prepolymer containing a carboxyl group and comprising a diisocyanate compound and a diol compound containing a polymeric polyol; with said method being characterized in further comprising a step (4) for diluting the urethane prepolymer using a monoalcohol-based solvent before the aqueous dispersion step (2) is performed.

[Claim 2] The method for producing a polyurethane resin aqueous dispersion according to claim 1, wherein the solubility of the monoalcohol-based solvent with respect to water at 25°C is 5 wt% or greater.

[Claim 3] The method for producing a polyurethane resin aqueous dispersion according to claim 1 or 2, wherein the monoalcohol-based solvent is a secondary or tertiary monoalcohol that does not have active hydrogen, and is reactive with isocyanate groups in addition to alcoholic hydroxyl groups.

[Claim 4] The method for producing a polyurethane resin aqueous dispersion according to claim 1, 2, or 3, wherein the amount in which the monoalcohol-based solvent is used is 3 to 30 wt% in relation to the urethane prepolymer.

[Claim 5] The method for producing a polyurethane resin aqueous dispersion according to claim 1, 2, 3, or 4, wherein the temperature of the dilution step (4) is 50°C or less.

[Claim 6] The method for producing a polyurethane resin aqueous dispersion according to claim 1, 2, 3, 4, or 5, wherein the neutralization step (1) is performed prior to the dilution step (4).

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a method for producing a polyurethane resin aqueous dispersion. The aqueous water-dispersible polyurethane resin obtained by the present invention can be used as a binder for paints, magnetic paints, printing inks, and the like; a coating agent for various substrates, such as artificial leather, plastic, glass,

metal, wood, paper, flooring, concrete, rubber, wovens, and nonwovens; an adhesive for a variety of materials, including artificial leather, plastic, glass, metal, wood, paper, flooring, concrete, rubber, wovens, and nonwovens; and the like.

[0002]

[Prior Art] Polyurethane resin is characterized by excellent pliability, demonstrates adhesion with a wide variety of substrates, and is often used for various binders, coatings, and adhesives. Although conventional polyurethane resin is primarily a solvent-based resin dissolved in an organic solvent, conversion to aqueous polyurethane resin is being actively pursued in an attempt to respond to social trends toward resource conservation, environmental protection, and stricter organic solvent control, and polyurethane resin aqueous dispersions are being put to practical use in certain fields.

[0003] The polyurethane resin aqueous dispersion being used today for practical purposes is produced by, for instance, dispersion in water and chain extension of a urethane prepolymer dissolved in an organic solvent that is inactive in relation to isocyanate groups, such as acetone or methyl ethyl ketone. Nevertheless, residue from organic solvents such as acetone and methyl ethyl ketone should not remain in the final product and these organic solvents are therefore removed by reducing pressure during the final steps of production. As a result, there is a problem with such a production method when compared to a method for producing solvent-type polyurethane resin in terms of prolonged production steps, low yield, and high cost.

[0004] A method for producing a polyurethane resin aqueous dispersion without using any organic solvent whatsoever has also been proposed (JP (Kokai) 4-31439). However, in addition to requiring a special reactor that is completely different from a conventional reactor, this production method poses practical difficulties in that the conditions for obtaining a polyurethane resin aqueous dispersion with stability are considerably restricted, and the like.

[0005]

[Problems to be Solved by the Invention] An object of the present invention is to provide a method for easily producing a polyurethane resin aqueous dispersion without using an organic solvent such as acetone or methyl ethyl ketone.

[0006]

[Means Used to Solve the Above-Mentioned Problems] The inventors performed intense studies to solve the above-mentioned problems and as a result, successfully completed the present invention upon discovering that when a specific urethane prepolymer is subjected to a neutralization step, water dispersion step, and chain-extension step, the above-mentioned problems can be solved by performing the aqueous dispersion step after the urethane prepolymer has been diluted using a monoalcohol-based solvent. They also discovered that any molecular design, such as a high-molecular-weight water-dispersible polyurethane resin, can be achieved under specific reaction conditions.

[0007] Specifically, the present invention relates to a method wherein an isocyanate-capped urethane prepolymer is manufactured and subsequently subjected to a step (1), in which the carboxyl groups are neutralized using a basic compound; and an aqueous dispersion step (2) and a chain-extending step (3), which are performed simultaneously or in succession, thereby producing a polyurethane resin aqueous dispersion. The prepolymer contains a carboxyl group and comprises a diisocyanate compound and a diol compound containing a polymeric polyol. The method being characterized in further comprising a step (4) for diluting the urethane prepolymer using a monoalcohol-based solvent before the aqueous dispersion step (2) is performed.

[0008]

[Embodiments of the Invention] The present invention first involves the production of an isocyanate-terminated urethane prepolymer that contains carboxyl groups and is composed of a diisocyanate compound and a diol compound containing a polymer polyol.

[0009] Examples of the polymer polyol component are conventional polymer polyols generally used for the production of polyurethane, including polyether polyols, such as polyethylene glycol, polypropylene glycol, or polyoxytetramethylene ether glycol obtained by ring-opening polymerization of, for instance, ethylene oxide, propylene oxide or tetrahydrofuran; polyester polyols obtained by dehydrocondensation of, for instance, a saturated or unsaturated conventional lower glycol, such as ethylene glycol, diethylene glycol, trimethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, pentanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, octanediol, 1,4-butanediol, dipropylene glycol,

bisphenol A, or hydrogenated bisphenol A, and a dibasic acid, such as adipic acid, maleic acid, fumaric acid, phthalic anhydride, isophthalic acid, terephthalic acid, succinic acid, oxalic acid, malonic acid, glutaric acid, pimelic acid, azelaic acid, sebacic acid, or suberic acid, or a corresponding acid anhydride; polyester polyols obtained by ring-opening polymerization of lactones such as ϵ -caprolactone and β -methyl- δ -valerolactone; other polycarbonate polyols; and polybutadiene glycols. Of these, preferred polyether polyols are those capable of reducing the urethane polymer viscosity and quickly dispersing in water, which is the dispersion medium of aqueous dispersion step (2). It is possible to substitute up to 5 mol% of the low-molecular-weight glycol component using a variety of polyols, such as glycerin, trimethylol propane, trimethylol ethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, pentaerythritol, and sorbitol.

[0010] There are no special restrictions to the number-average molecular weight of the polymer polyol, but in terms of pliability of the resulting polyurethane resin film, it is usually 500 or greater, preferably 700 or greater, and in terms of water dispersibility of the urethane prepolymer and drying performance of the resulting polyurethane resin, it is 10,000 or less, preferably 5,000 or less.

[0011] According to the present invention, carboxyl groups are introduced to a urethane polymer; therefore, usually a diol containing carboxyl groups is used as a diol compound. Examples of diols containing carboxyl groups are α,α' -dimethylolalkanoic acids (such as glyceric acid, dimethylpropionic acid, dimethylolbutanoic acid, 2,2-dimethylolpentanoic acid), dioxymaleic acid, dioxyfumaric acid, tartaric acid, 2,6-dioxybenzoic acid, 4,4-bis(hydroxyphenyl)valeric acid, and 4,4-bis(hydroxyphenyl)butyric acid), and compounds obtained by using these diols containing carboxyl groups as the initiator for ring-opening polymerization of a lactone, such as ϵ -caprolactone, γ -butyrolactone, and γ -valerolactone. These diols containing carboxyl groups are usually used as the above-mentioned polymer polyol and as the diol component for producing the urethane prepolymer, but when a diol containing carboxyl groups such as one obtained by ring-opening polymerization of a lactone is itself used as the polymer polyol, it is also possible to use this diol containing carboxyl groups alone as the diol compound.

[0012] Aromatic, aliphatic, and alicyclic diisocyanates can be used as the diisocyanate compound. Examples are 1,5-naphthylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-diphenyldimethylmethane diisocyanate, 4,4'-dibenzyl isocyanate, dialkyldiphenylmethane

diisocyanate, tetralkyldiphenylmethane diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, tolylene diisocyanate, butane-1,4-diisocyanate, hexamethylene diisocyanate, isopropylene diisocyanate, methylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, cyclohexane-1,4-diisocyanate, xylylene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 1,3-bis(isocyanatemethyl)cyclohexane, methylcyclohexane diisocyanate, *m*-tetramethylxylylene diisocyanate, and dimer isocyanates obtained by converting the carboxyl groups of dimer acid to isocyanate groups.

[0013] The production of an isocyanate-terminated urethane prepolymer containing carboxyl groups is accomplished by reacting the above-mentioned diol compound and diisocyanate compound such that the equimolar amount of diisocyanate compound in terms of isocyanate groups exceeds the equimolar amount of diol compound in terms of hydroxyl groups. The reaction is usually performed in the absence of a solvent, and the reaction temperature, reaction time, and presence of a urethane catalyst can be determined as needed in accordance with reactivity. Although there are no special restrictions to the amount of diol containing carboxyl groups in the diol compound, it is preferred that the diol containing carboxyl groups be used such that the acid value per gram of resin solid content of the polyurethane resin be 5 or greater in order to obtain a polyurethane resin aqueous dispersion with good dispersion stability, while in terms of water resistance of the resulting polyurethane, it is preferred that the diol containing carboxyl groups be used such that the acid value is 100 or less.

[0014] Next, the resulting urethane prepolymer is subjected to a neutralization step (1) wherein the carboxyl groups are neutralized by a basic compound, and an aqueous dispersion step (2) that is performed simultaneously or in succession with a chain-extending step (3) to obtain a polyurethane resin aqueous dispersion. However, according to the present invention, a step (4) for diluting the urethane prepolymer using a monoalcohol-based solvent is performed before the aqueous dispersion step (2).

[0015] The urethane prepolymer is subjected to the dilution step (4) before the aqueous dispersion step (2) in order to reduce the viscosity of the urethane prepolymer, which is high when in a solvent-free state, and to use the hydrophilic property of the monoalcohol-based solvent in order to increase the speed of dispersion in water, which is the dispersion vehicle of the aqueous dispersion step (2). Moreover, it is not necessary to remove the monoalcohol-based

solvent from the final product obtained from the polyurethane resin as it is with an organic solvent such as acetone or methyl ethyl ketone. It should be noted that in cases in which the dilution step (4) is not performed prior to the aqueous dispersion step (2), even when a mixture of water and a monoalcohol-based solvent is used as the dispersion medium of aqueous dispersion step (2), the high-viscosity urethane prepolymer will not quickly and uniformly mix with the water, there will be an increase in molecular weight as a result of reaction between some of the water and isocyanate groups, and it will not be possible to obtain a stable polyurethane resin aqueous dispersion.

[0016] A variety of monoalcohol-based solvents can be use for the dilution step (4), but it is preferred that one having a solubility in water at 25°C of 5 wt% or greater be used for quick dispersion in the water.

[0017] Moreover, a secondary or tertiary monoalcohol having a slow reaction speed with the terminal isocyanate groups in the urethane prepolymer is preferred. A monoalcohol-based solvent not having active hydrogen showing reactivity with isocyanate groups other than alcoholic hydroxyl groups is preferred. Such a monoalcohol-based solvent will consume little of the terminal isocyanate groups in the urethane prepolymer during the dilution step (4), and it will not join the prepolymer chains to one another to increase molecular weight. Therefore, any molecular design, a high-molecular-weight water-dispersible polyurethane resin produced by chain extension step (3), becomes possible; it is possible to quickly disperse the alcohol in water during water dispersion step (2); and a stable polyurethane resin aqueous solution can be obtained.

[0018] Examples of monoalcohol-based solvents that satisfy the above-mentioned conditions are isopropyl alcohol, isobutyl alcohol, *sec*-butyl alcohol, *tert*-butyl alcohol, *sec*-amyl alcohol, and diacetone alcohol.

[0019] The monoalcohol-based solvent used in the dilution step (4) can be used alone, or a combination of two or more can be used. There are no special restrictions to the amount used, but it is usually 3 wt% or more, preferably 10 wt% or more, per urethane prepolymer. Moreover, in order to prevent a reaction between the terminal isocyanate groups of the urethane prepolymer and the hydroxyl groups of the alcohol-based solvent, the amount of monoalcohol-based solvent used is 30 wt% or less, preferably 25 wt% or less, in terms of prepolymer. Although there are no special restrictions to the temperature of the dilution step (4), 50°C or lower is preferred because

a slow reaction speed between the isocyanate groups of the urethane prepolymer and the alcoholic hydroxyl groups of the alcohol-based solvent will be obtained. The temperature of the dilution step (4) is usually normal temperature or higher.

[0020] According to the present invention, the dilution step (4) is performed before the aqueous dispersion step (2), but there is no particular restriction to the order of each step other than the dilution step (4); i.e., the neutralization step (1) and the aqueous dispersion step (2) and chain extension step (3) that are performed simultaneously or in succession. Consequently, it is possible to perform the neutralization step (1) before or after the aqueous dispersion step (2) and chain extension step (3) are performed simultaneously or in succession, or together with the aqueous dispersion step (2). For instance, it is preferred that the neutralization step (1) be performed before the aqueous dispersion step (2) in order to quickly disperse the urethane prepolymer during the aqueous dispersion step (2) and obtain a stable polyurethane aqueous dispersion. Moreover, it is preferred that the dilution step (4) be performed after the neutralization step (1) because there is a tendency toward delayed reaction between the isocyanate groups of the urethane prepolymer and the alcoholic hydroxyl groups of the alcohol-based solvent.

[0021] Examples of the basic compound used for neutralization of the carboxyl groups in the urethane prepolymer during neutralization step (1) include alkali metals, such as potassium hydroxide and sodium hydroxide, ammonia, and tertiary amines, such as trimethylamine, triethylamine, triisopropylamine, tributylamine, triethanolamine, *N*-alkyldiethanolamine, and *N,N'*-dialkylmonoethanolamine. These basic compounds can be used alone or in combinations of two or more. The basic compound is preferably used in an amount that is 0.5 to 1.5 molar equivalents in terms of 1 molar equivalent of carboxyl groups contained in the prepolymer in order to neutralize the carboxyl groups (hereafter represented as a neutralization rate of 50 to 150%). If the neutralization rate is lower than 50%, the dispersion stability of the resulting polyurethane resin aqueous dispersion will be insufficient, and if it is greater than 150%, there will be a tendency toward an increase in system viscosity during aqueous dispersion. Although there are no special restrictions to the neutralization temperature, it is usually 20 to 70°C.

[0022] There are no special restrictions to the aqueous dispersion step (2). For instance, it is possible to use a method whereby water for dispersion is added to the urethane prepolymer

diluted by alcohol-based solvent, or a method that is the opposite thereof, whereby the urethane prepolymer diluted in water is added for dispersion.

[0023] Moreover, chain-extension step (3) is performed using a chain extender and when necessary, a chain extension inhibitor. Examples of chain extenders are conventional low-molecular-weight glycols described under the above-mentioned description of the polyester diols; water; and amines such as ethylene diamine, propylene diamine, hexamethylene diamine, diethylene triamine, trimethylene tetramine, isophoronediamine, and dicyclohexylemethane-4,4-diamine. Other examples are diamines having hydroxyl groups in their molecules, such as 2-hydroxyethyl ethylenediamine, 2-hydroxyethyl propylenediamine, di-2-hydroxyethyl ethylenediamine, di-2-hydroxyethyl propylenediamine, 2-hydroxypropylethylene diamine, and di-2-hydroxypropyl ethylenediamine; and dimer diamines wherein the carboxyl groups of the dimer acid are converted to amino groups. Examples of chain extension inhibitors are monoamines such as monobutylamine and dibutylamine; monoamines having hydroxyl groups such as monoethanolamine and diethanolamine; and monoalcohols having primary alcoholic hydroxyl groups such as ethanol and *n*-butanol.

[0024] Aqueous dispersion step (2) and chain extension step (3) are performed simultaneously or in succession; therefore, the chain extender and chain extension inhibitor used as necessary can be pre-added to the water that is used for aqueous dispersion of the urethane prepolymer, or they can be added after aqueous dispersion of the urethane prepolymer. It should be noted that in addition to being added during or after aqueous dispersion of the urethane prepolymer, the chain extension inhibitor can be added before or after the neutralization step (1) or dilution step (4).

[0025] The average molecular weight of the resulting aqueous dispersible polyurethane resin can be determined as needed based on the purpose of use, but it is preferably a weight-average molecular weight of 5,000 or greater when used in a field requiring resin film strength.

[0026] There are no particular restrictions to the solid concentration or viscosity of the polyurethane resin aqueous solution of the present invention, and they can be determined as needed taking into consideration operation performance, and the like when used. It is usually preferred for practical use that the solid concentration be brought to within a range of 15 to 60 wt% and viscosity be brought to within a range of 10 to 100,000 cps/25°C.

[0027] When the polyurethane resin aqueous solution of the present invention is used for any of variety of reasons, water and various pigments, and the like as necessary can be added and mixed or dispersed in the polyurethane resin aqueous dispersion of the present invention, and antiblocking agents, plasticizers, and other additives can be added as needed to prepare the above-mentioned binder, coating, or adhesive composition.

[0028]

[Effect of the Invention] According to the present invention, it is possible to easily produce a polyurethane resin aqueous dispersion without going through an inefficient solvent-removal step. Moreover, by using specific conditions for each step, any molecular design, such as a high-molecular-weight water-dispersible polyurethane resin, becomes possible, and a production method of excellent reproducibility is obtained. Moreover, it is possible to obtain a polyurethane resin aqueous dispersion of excellent stability by using specific conditions for each step.

[0029]

[Working Examples] The present invention will now be described in specific terms using production examples, working examples, and comparative examples, but the present invention is not limited to these working examples. The parts and % are all by weight.

[0030] Working Example 1

25.3 parts of dimethylol butanoic acid and 334.5 parts of polytetramethylene ether glycol having a number-average molecular weight of 2,000 were introduced to a reactor having a mixer, thermometer, cooling tube, and nitrogen gas tube, and the dimethylol butanoic acid was completely dissolved over a one-hour period at 100°C under a nitrogen gas current. After cooling to 85°C, 120.2 parts of isophorone diisocyanate was introduced and reacted for five hours at 85°C. 480 parts of isocyanate-terminated urethane prepolymer was obtained. 17.3 parts of triethylamine was added to this urethane prepolymer at 50°C, and after neutralization (neutralization rate of 100%), 84.7 parts of isopropyl alcohol was added to produce a uniform isopropyl alcohol solution of a urethane prepolymer. Next, 1,078 parts of water was added for dispersion while stirring at 40°C, then 23.2 parts of isophorone diamine was added, the mixture was reacted for three hours at 40°C, and polyurethane resin aqueous dispersion A was obtained. This aqueous dispersion A had a resin solid content of 30%, a viscosity of 25 cps/25°C, and a pH of 8.2, and the dry resin had a resin acid value of 20.

[0031] Working Example 2

128.3 parts of Plaxel 205BA (dimethylol butanoic acid ϵ -caprolatone addition product: number-average molecular weight 500; Daicel Chemical Industries, Ltd.), 221.2 parts of polypropylene glycol having a number-average molecular weight of 2,000, and 130.5 parts of isophorone cyanate were introduced, a reaction was performed for five hours at 85°C under a nitrogen gas current, and 480 parts of an isocyanate-terminated urethane prepolymer was obtained. 25.9 parts of triethylamine was added to this urethane prepolymer at 50°C and after neutralization (neutralization rate of 100%), 120.0 parts of isopropyl alcohol were added to produce a uniform isopropyl alcohol solution of a urethane prepolymer. Next, 1,147 parts of water and a mixture of 18.5 parts of isophorone diamine and 1.9 parts of diethylene triamine were added while stirring; dispersed; and subjected to reaction at 35°C for 3 hrs, resulting in polyurethane resin aqueous dispersion B. This aqueous dispersion B had a resin solid content of 28%, a viscosity of 380 cps/25°C, and a pH of 8.3, and the dry resin had a resin acid value of 29.

[0032] Working Example 3

38.0 parts of methylol butanoic acid, 149.1 parts of polypropylene glycol having a number-average molecular weight of 3,000, and 149.1 parts of polybutylene adipate having a number-average molecular weight of 2,000 were introduced into the same reactor used in Working Example 1, and the dimethylol butanoic acid was completely dissolved over a one-hour period at 100°C under a nitrogen gas current. Next, after cooling to 85°C, 143.8 parts of isophorone diisocyanate was introduced, a reaction was performed for five hours at 85°C under a nitrogen current, and 480 parts of isocyanate-terminated urethane prepolymer was obtained. 25.9 parts of triethylamine was added to this prepolymer at 50°C and after neutralization (neutralization rate of 100%), 53.3 parts of *tert*-butyl alcohol was added to produce a uniform *tert*-butyl alcohol solution of a urethane prepolymer. Next, 1,106 parts of water and a mixture of 21.1 parts of isophorone diamine and 3.6 parts of diethylene triamine were added while stirring and dispersed at 45°C, the mixture was reacted for three hours at 45°C, and polyurethane resin aqueous dispersion C was obtained. This aqueous dispersion C had a resin solid content of 30%, a viscosity of 110 cps/25°C, and a pH of 8.0, and the dry resin had a resin acid value of 29.

[0033] Comparative Example 1

Other than the fact that Working Example 3 was changed such that *tert*-butyl alcohol was mixed with the water and the isophorone diamine and diethylene triamine and added without

diluting the prepolymer with the *tert*-butyl alcohol after neutralization by the triethyl amine but prior to aqueous dispersion, an attempt was made to produce an aqueous dispersion of a polyurethane resin by the same method as in Working Example 3, but a uniform dispersion was not obtained during aqueous dispersion. When stirring was stopped and the mixture was set aside, it quickly separated.

[0034] Comparative Example 2

1,163 parts of water was added while stirring at 40°C without diluting the prepolymer with isopropyl alcohol after neutralization by triethylamine but before aqueous dispersion in Working Example 2 in an attempt to produce an aqueous dispersion of the polyurethane resin, but a uniform dispersion was not obtained during aqueous dispersion. When stirring was stopped and the mixture was set aside, it quickly separated.

[0035] The aqueous dispersions of polyurethane resin obtained in Working Examples 1 through 3 were evaluated in terms of the following items. Table 1 shows the evaluation results.

[0036] Weight-average molecular weight: GPC determination in terms of polystyrene.

[0037] Stability: Once the aqueous dispersion of polyurethane resin had been set aside for 30 days at 40°C, changes in status were evaluated by the following criteria:

○: No change.

✕: Separation or precipitation.

[0038]

[Table 1]

	Weight-average molecular weight	Stability
Working Example 1	25,000	○
Working Example 2	19,000	○
Working Example 3	24,000	○